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In January 1978, a study was undertaken at Jones State Forest, 38 miles north of Houston, Texas, to determine the concentrations of non-methane hydrocarbons, methane, and carbon monoxide; to detail the composition of hydrocarbons (especially of the vegetation); and to discover the sources of non-methane hydrocarbons. Thirteen 3-hour integrated Tedlar bag samples and five grab samples using stainless steel cans were collected over a 39-hour period. The samples were returned to the Research Triangle Park laboratory for analysis, where the can samples showed lower non-methane hydrocarbon concentration values that did the bag samples. Sources of paraffins (72% of the non-methane hydrocarbons) and the other hydrocarbons were found to be: vehicular exhaust (35%), the forest's vegetation (2%), the city of Houston (22%), and the region between Houston and the forest (32%). Isoprene and alpha-pinene were the vegetative hydrocarbons noted, with the latter showing a destinctive 24-hour cycle of concentration variation.

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NON-URBAN HYDROCARBON CONCENTRATIONS IN AMBIENT AIR NORTH OF HOUSTON, TEXAS

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ABSTRACT

In January 1978, a study was undertaken at Jones State Forest, 38 miles north of Houston, Texas, to determine the concentrations of non-methane hydrocarbons, methane, and carbon monoxide; to detail the composition of hydrocarbons (especially of the vegetation); and to discover the sources of non-methane hydrocarbons. Thirteen 3-hour integrated Tedlar bag samples and five grab samples using stainless steel cans were collected over a 39-hour period. The samples were returned to the Research Triangle Park laboratory for analysis, where the can samples showed lower non-methane hydrocarbon concentration values that did the bag samples. Sources of paraffins (72% of the non-methane hydrocarbons) and the other hydrocarbons were found to be: vehicular exhaust (35%), the forest's vegetation (2%), the city of Houston (22%), and the region between Houston and the forest (32%). Isoprene and alpha-pinene were the vegetative hydrocarbons noted, with the latter showing a destinctive 24-hour cycle of concentration variation.

This report covers a period from January to April 1978 and work was completed as of December 1978.

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SECTION 1

INTRODUCTION

The importance of vegetative hydrocarbons in the photochemical production of ozone is an ongoing subject of controversey and debate. The issue has been defined and discussed by Dimitriades and Altshuller (1) and reviewed and analyzed by Coffey and Westberg (2,3). The data concerning photochemical reactivities, emission rates, and ambient concentrations of vegetative hydrocarbons are the evidence upon which analyses and opinions are based. This report concerns the ambient concentration component of the issue.

Whitehead and Severs reported a mean ambient non-methane total hydrocarbon (NMTHC) concentration of 8.7 ppm for 35 morning samples collected at W.G. Jones State Forest (JSF), a 1700 acre tract located in Montgomery County 38 miles north of Houston, Texas. They concluded that the "high NMTHC levels observed were produced by the forest vegetation" (4). The results of Whitehead and Severs seem to run counter to the prevailing evidence concerning ambient vegetative hydrocarbon concentrations. Westberg reviewed the available ambient concentration data and concluded that natural hydrocarbon concentrations are of the order of a few ppb carbon (ppbC), even in forested regions (5). The ambient alpha-pinene concentrations measured by this laboratory at a loblolly pine plantation in central North Carolina were only a few ppbC, ranging from 0.6 to 13 for over 300 samples collected above the canopy during midday. The highest concentration observed within the canopy itself was 55 ppbC during night inversion conditions. Even when limbs were enclosed in Teflon bags - a method for determining vegetative emission rates (6) - the NMTHC concentrations rarely exceeded 8.7 ppm.

Since Whitehead and Severs used a total hydrocarbon analyzer for their investigation, they had no means for determining the specific hydrocarbons contributing to their NMTHC values. In order to determine the specific hydrocarbons and their contributions to the NMTHC burden at JSF a three-day sampling program was undertaken. This report presents the results of that study.

SECTION 2

CONCLUSIONS

The conclusions herein concern the ambient air concentrations, composition, and sources of hydrocarbons at JSF. Because of the limited nature of the sampling program, the conclusions are valid only for the period of the study when the wind was from a southerly direction.

The NMTHC concentrations at JSF ranged from 0.1 to 0.5 ppm and consist primarily of paraffins. The NMTHC composition during this study was 72% paraffin, 18% aromatic, 6% olefin, 2% acetylene, and 2% vegetative.

The vast majority of NMTHC in the air of JSF, 89% in this study were transported there from outside sources. The sources can be divided into two main categories: vehicular and non-vehicular. In this study, vehicular sources accounted for 35% and non-vehicular sources accounted for 54% of Jones State Forest NMTHC. Of the non-vehicular hydrocarbons 41% were due to Houston sources, and 59% were due to sources north of Houston. Refinery and natural gas emissions appear to account for most of the non-vehicular hydrocarbons.

The vegetative hydrocarbon concentrations at JSF were low; they were less than 10 ppbC and represented only 2% of the NMTHC burden.

SECTION 3

RECOMMENDATIONS

Background sampling at JSF when the wind is from the northwest is desirable in order to better ascertain the effects of Houston on JSF NMTHC.

Sampling of geogenic oil and natural gas seeps in the Houston area is suggested in order to estimate the magnitude of natural petroleum emissions.

Sampling of gaseoline, refinery emissions, and commercial and geogenic natural gas in the Houston area is recommended in order to perform a thorough source reconcilation for Houston similar to that done for Los Angeles by Mayrsohn and Crabtree (7).

SECTION 4

EXPERIMENTAL

LOCATION

Jones State Forest is located one mile west of Interstate Highway 45 on Farm to Market Road (FM) 1488, and five miles southwest of Conroe, the nearest town. Figure 1 shows its location relative to Houston. It is operated by the Texas Forest Service for research and recreation (picnicking and camping). The predominant vegetation is loblolly pine.

SAMPLING METHODS

The JSF sampling consisted of diurnal sampling using bags, and grab sampling using steel cans. Thirteen, 3-hour integrated samples were collected in Tedlar bags from January 4 to January 6, 1978. Five grab samples were collected in stainless steel cans on January 5. In addition to the JSF sampling, two samples of commercial natural gas from the Houston Medical Center were collected in cans during March 1978.

Samples were collected at two sites within JSF (Figure 2). All of the thirteen diurnal samples and three of the can samples were collected at a picnic area about 100 meters from FM 1488. This site was the only location with electricity for operating a continuous sampling system, yet it was not an ideal site because of the close proximity of FM 1488, a rural paved road with moderate traffic. However, southerly winds kept the road downwind of the picnic site during the entire study, which minimized the impact of local automobile pollution. The second site was deeper in the forest away from the potential impact of the road. Two can samples were collected there by means of a battery operated pump.

Diurnal sampling was performed from 1500 CST, January 4, to 0600 CST, January 6, 1978. A sequential sampler as diagrammed in Figure 3 was used to collect 3-hour integrated samples in 10 liter capacity 2 mil Tedlar bags; construction of the bags is described elsewhere (8). The bags were leak-tested by evacuation prior to shipment to Houston, and by subsequent visual inspection just before use. If air had leaked into a bag it was not used. Just prior to attachment to the sampler, each bag was spiked with 15 ml of a 38 ppm mixture of nitric oxide in nitrogen to destroy any ozone present in the air being sampled, in order to prevent reaction with the hydrocarbons in the samples. Only 5 liters of sample were collected to allow for expansion during the return flight to Research Triangle Park. Upon return three very deflated bags were presumed to have leaked and were not analyzed.

LOCATION OF JONES STATE FOREST

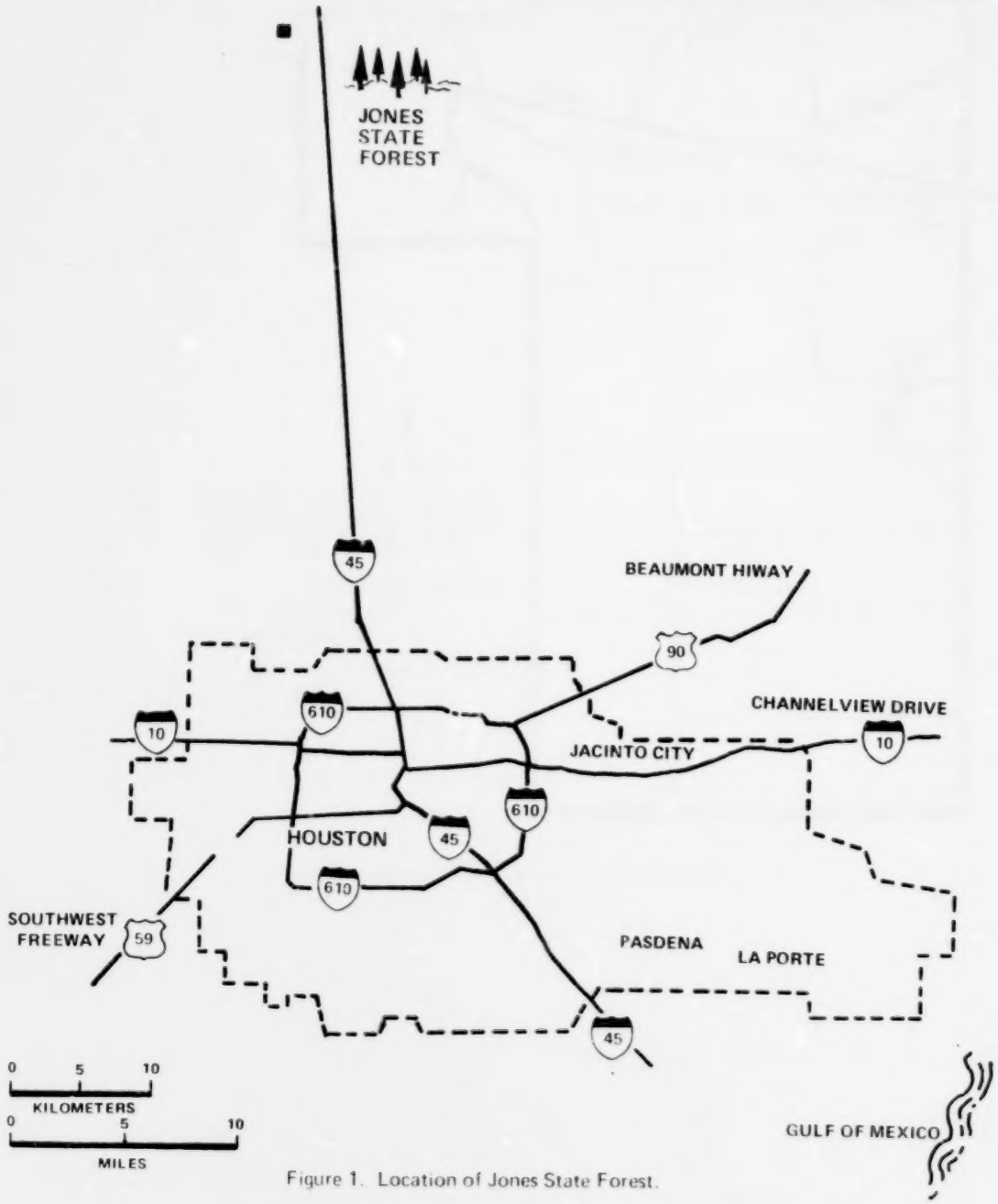

Figure 1. Location of Jones State Forest.

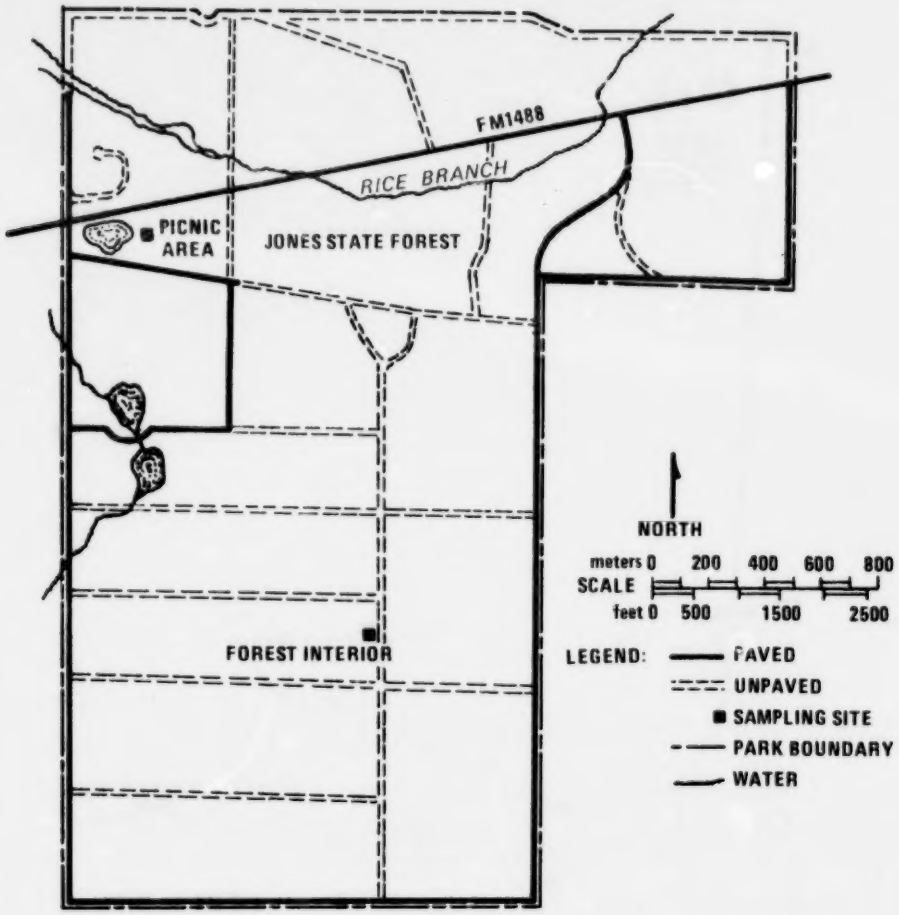

Figure 2. Sampling sites at Jones State Forest.

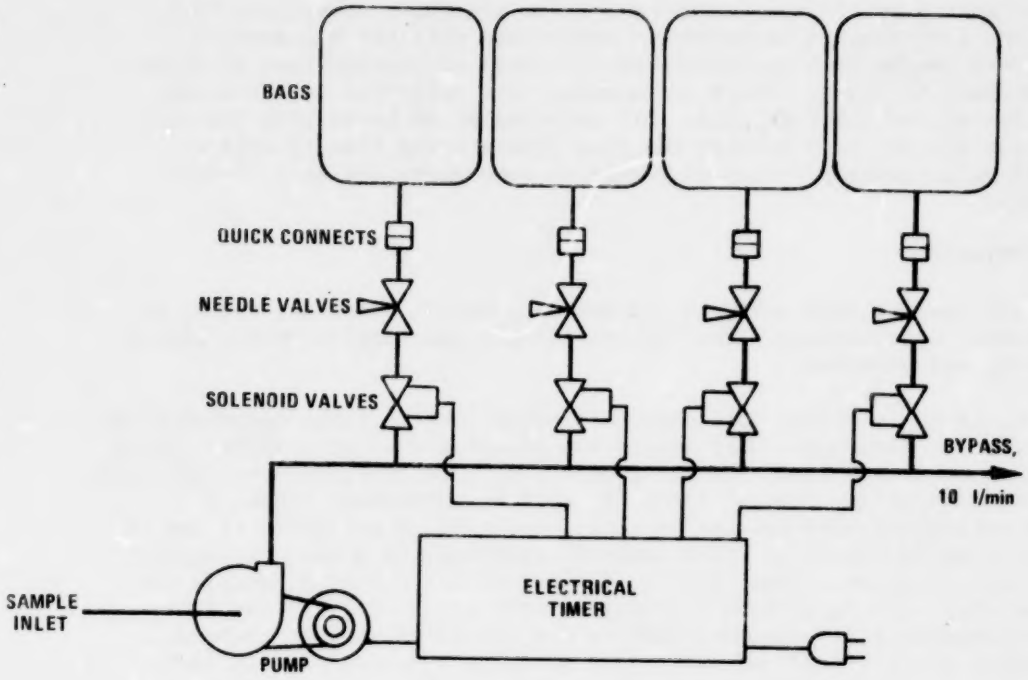

Figure 3. Sequential ambient air sampler.

Five internally electropolished 4.5 liter stainless steel cans were used for the grab samples to provide a comparison with the bag samples. The cans were purged with approximately 50 liters of pre-purified nitrogen before shipment to Texas. Three can samples were collected at the picnic site and two at the interior site. All were collected by purging the cans with ambient air for five minutes and then pressurizing them to approximately 15 psig, using a Teflon diaphragm dc pump energized by a 12-volt car battery.

ANALYSIS METHODS

The JSF samples were analyzed for methane, carbon monoxide, and C_2 to C_{10} individual hydrocarbons. The Houston natural gas samples were analyzed for C_1 to C_5 hydrocarbons.

The C_2 to C_{10} analyses were performed using three columns equipped with flame ionization detectors; each sample was analyzed once per column. Prior to injection on each column, 400 ml of sample were concentrated by a cryogenic preconcentration step. Table 1 lists the columns, cryogenic traps, and injection technqiues used for the C_2 to C_{10} analyses; a schematic of the GC system is shown in Figure 4. Each analysis required two steps: cryogenic trapping and injection. When value V_1 (Figure 4) was actuated, sample air was routed from the bag through a cryogenic trap into the 2.5 liter tank, where the pressure difference was used to fix the volume of air trapped. Liquid oxygen was the cryogen. Actuation of value V_2 routed carrier gas through the trap for the injection. The trap substrates and injection techniques were determined by the nature of the compounds to be analyzed.

Methane and carbon monoxide determinations were performed on a Beckman 6800 air quality chromatograph.

The natural gas analyses were performed on the same silica gel column that was employed for the ambient C_2 to C_5 aliphatics analyses. However, cryogenic preconcentration was not required for the natural gas analyses.

All GC detector outputs were recorded on strip chart recorders, while a Hewlett Packard digitizer was used to measure peak areas and heights from the strip chart chromatograms. Response factors determined from analyses of known concentration compounds were used to convert the area or height measurements to concentrations. Detailed results of the analyses are contained in Appendix A.

TABLE 1. GC COLUMNS AND METHODS FOR HYDROCARBON ANALYSES

Analysis	GC Column	Cryogenic Trap	Injection Technique
C_2 to C_5 and natural gas	2.4 m X 3 mm SS with 60/80, nitric acid washed, grade 58 silica gel at room temperature. He carrier gas	30 cm X 3 mm SS with 10% carbowax 1540 on 60/80 Gas Chrom Z	Front flush trap at room temperature for two minutes
C_4 to C_8	91 m X 1.5 mm i.d. open tubular copper column coated with dibutylmaleate at ice water temperature. He carrier gas	30 cm X 3 mm SS with 10% carbowax 1540 on 60/80 Gas Chrom Z	Front flush trap in room temperature water for 25 seconds
C_6 to C_{10}	91 m X 1.5 mm i.d. open tubular copper column coated with a mixture of m-bis (m-phenoxy phenoxy) benzene (MBMA) and Apiezon L grease at 65°C. He carrier gas	30 cm X 3 mm SS with 60/80 glass beads	Back flush trap in hot (90°C) water for 45 seconds

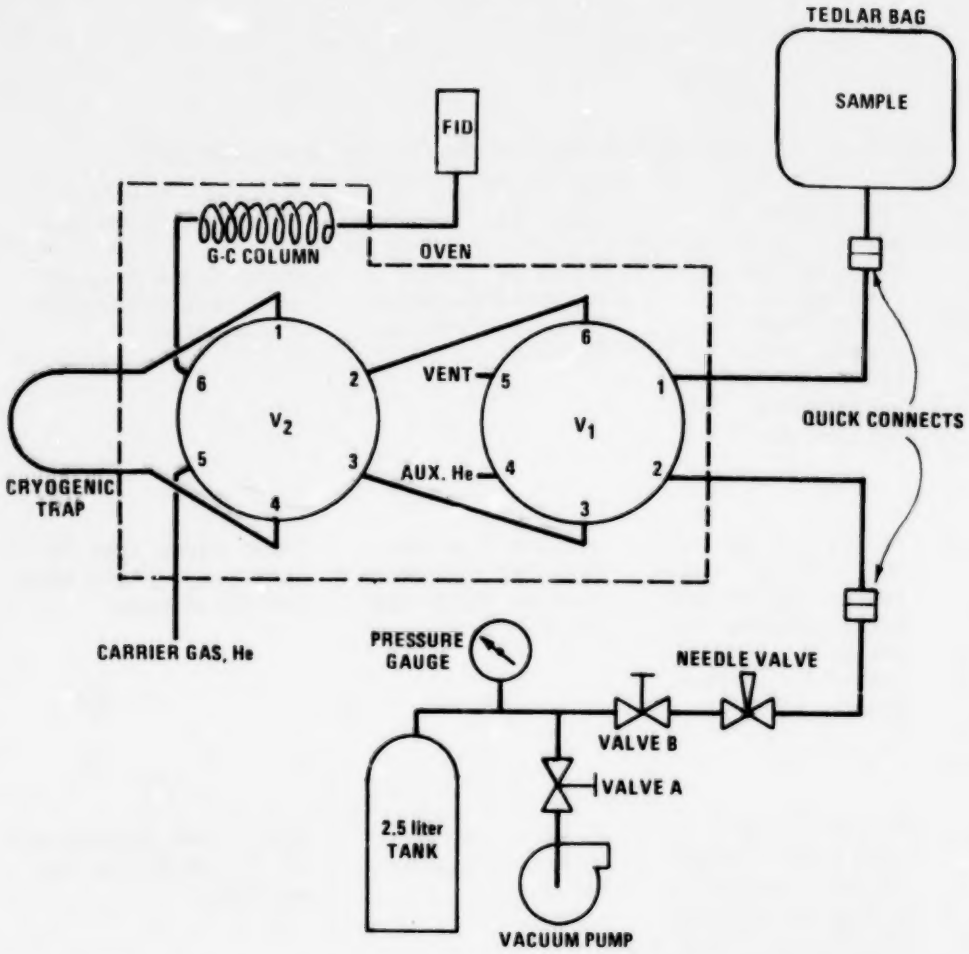

Figure 4. Hydrocarbon analysis chromatographic system.

SECTION 5

RESULTS AND DISCUSSION

This section of the report discusses the following questions: What are the CH_4, NMTHC, and CO concentrations in JSF and how do they compare with the measurements of Whitehead and Severs? Do the bag and can sample results differ? What is the NMTHC composition at Jones State Forest? What are the sources of JSF NMTHC? and What are the vegetative hydrocarbon concentration levels in Jones State Forest?

NMTHC, CH_4, CO RESULTS

A summary of the NMTHC, CH_4 and CO results of this study is presented graphically in Figure 5. The NMTHC concentrations were derived by summing the individual hydrocarbon concentrations. The comparison of the results of this study and those of Whitehead and Severs are shown in Table 2. Although the CO measurements of the two studies agree quite closely, the NMTHC values are very disparate.

TABLE 2. COMPARISON OF NMTHC AND CO MEASUREMENTS IN JSF

Pollutant	Mean Concentration, ppm	
	Whitehead and Severs	This study
CO	0.60 ± 0.15	0.63 ± 0.16 (bags) 0.47 ± 0.14 (cans)
NMTHC	8.7	0.306 ± 0.096 (bags) 0.184 ± 0.069 (cans)

BAG/CAN DIFFERENCES

Observation of Figure 5 suggests that although the CH_4 and CO differences between the bag and can samples are minimal, the can NMTHC values seem significantly lower than those of the bags. All but one of the can NMTHC concentrations were lower than the lowest bag NMTHC value. A more detailed examination of the differences between the bags and cans is provided by Table 3, which compares the bag and can median concentrations for various groups and individual hydrocarbons. Most of the hydrocarbons, though not all, were much higher in the bags than the cans. Ethane, propane, alpha-pinene, and other aromatics showed no significant difference, while the oxygenates (acetaldehyde,

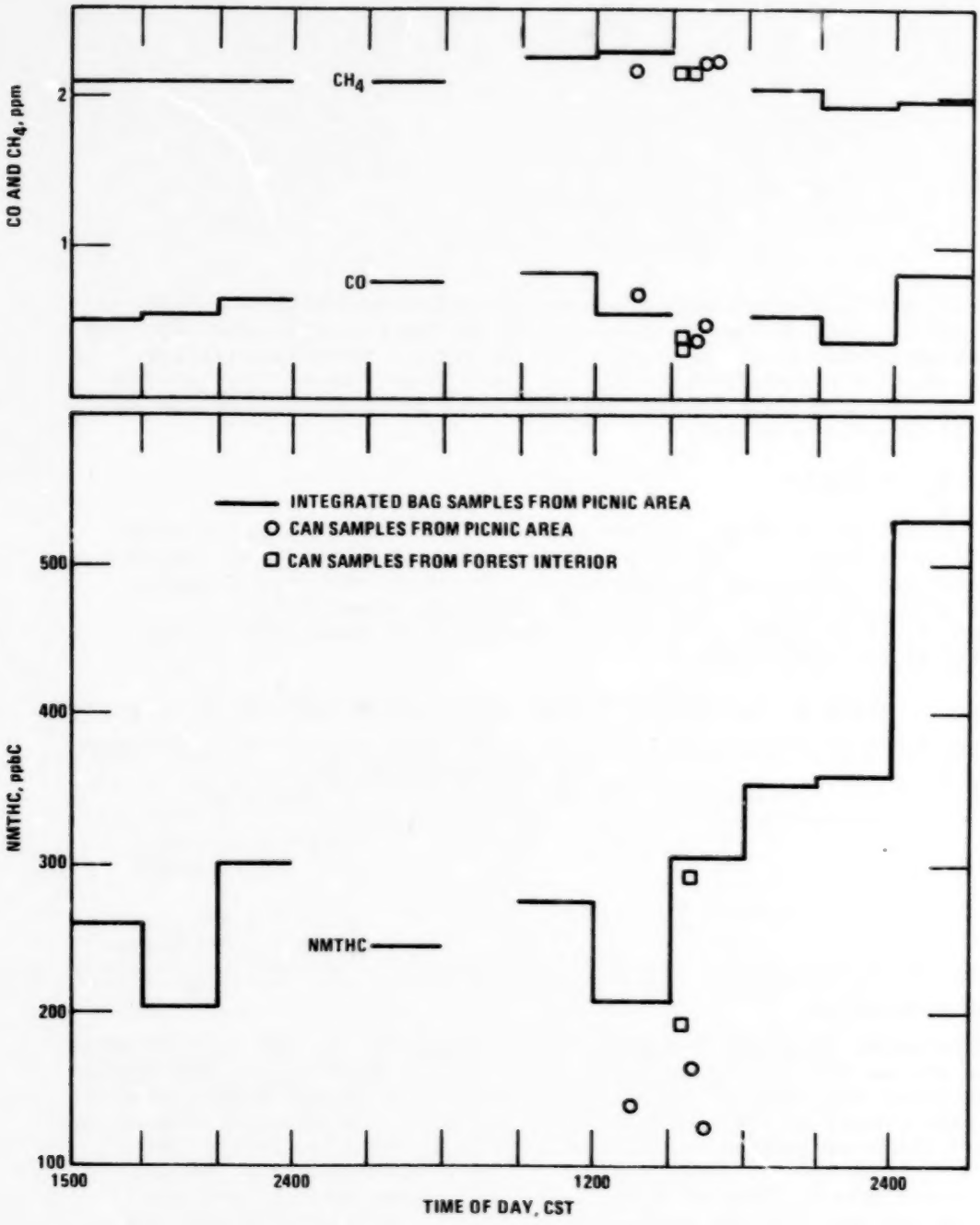

Figure 5. Jones State Forest NMTHC, CH_4, AND CO concentration results for January 4-6, 1978.

TABLE 3. DETAILED COMPARISON OF JSF CAN AND BAG SAMPLES

Compound	Median Concentration, ppbC	
	5 Can samples	10 Bag samples
Ethane	27.3	27.6
Propane	17.5	21.6
Isobutane	6.2	13.5
N-butane	9.7	20.2
Isopentane	5.9	14.8
N-Pentane	3.6	11.1
Cyclopentane	0.6	1.4
2-Methylpentane	1.2	4.3
3-Methylpentane	0.9	3.2
N-hexane	1.6	4.1
Other paraffins	11.4	42.1
Ethylene	4.2	8.9
Propylene	1.0	5.1
C-4 olefins	1.9	10.6
C-5 olefins	0.6	1.2
Toluene	4.7	10.9
Xylene	5.3	10.9
Ethylbenzene	1.0	2.8
Other Aromatics	13.1	16.8
Acetylene	2.6	3.6
Alpha-pinene	3.0	3.2
Acetaldehyde	10.7	7.9
Propionaldehyde	14.2	n.d.
Acetone	6.9	5.7
Carbon monoxide	420	570

acetone, propionaldehyde) were considerably greater in the cans than the bags. The oxygenate concentrations in the cans were so great that they were probably not representative of their true values in JSF.

The median oxygenate concentration for can samples was 33 ppbC, while the median concentration for bags was 12.3 ppbC. A review of the results of previous samples stored in the same five cans that were used at JSF is shown in Table 4. The median oxygenate concentration of previous samples was also a high 35 ppbC. One can in particular showed very high oxygenate concentrations, 103 and 82 ppbC, for the two samples suggesting an oxygenate artifact effect which might vary from can to can. Further experiments were conducted to investigate this phenomenon.

TABLE 4. OXYGENATE CONCENTRATIONS OF JSF CAN SAMPLES COMPARED WITH THE PREVIOUS SAMPLES FROM THE SAME CANS

	Σ Oxygenates, ppbC	
Can number	Jones State Forest	Previous sample
1	21	23
2	103	82
3	49	36
4	33	35
5	10	32
Median ± s	33 ± 40	35 ± 25

When zero grade nitrogen was stored in the cans no buildup of oxygenates was observed; however, when ambient air was stored in two cans and two Tedlar bags, all containers showed a significant buildup of oxygenates over a ten day storage period (acetaldehyde results are graphed in Figure 6). This evidence suggests that the JSF oxygenate determinations were biased high and should not be included in the NMTHC summations. These findings concerning the oxygenates however do not help to explain the fact that the NMTHC values were higher in the bags than the cans.

The NMTHC difference must be due to the loss of hydrocarbons on the can surfaces, the addition of hydrocarbons to the bags by permeation or leaks, or a combination of the two. Surface deposition should be evidenced by an increasing difference between the bag and can concentrations as the molecular weights increase, but the data of Table 3 do not show such a trend. The minimal differences that the bags and cans show in alpha-pinene and the other aromatics suggest that these hydrocarbons are not deposited onto surfaces. With the lack of clear surface deposition evidence, it must be concluded that the bags were contaminated through leaks or permeation (probably permeation of fuel vapors during the return flight), indicating that the bag results are an overestimate of NMTHC, and that can results minus oxygenate concentrations are the best estimates of Jones State Forest NMTHC.

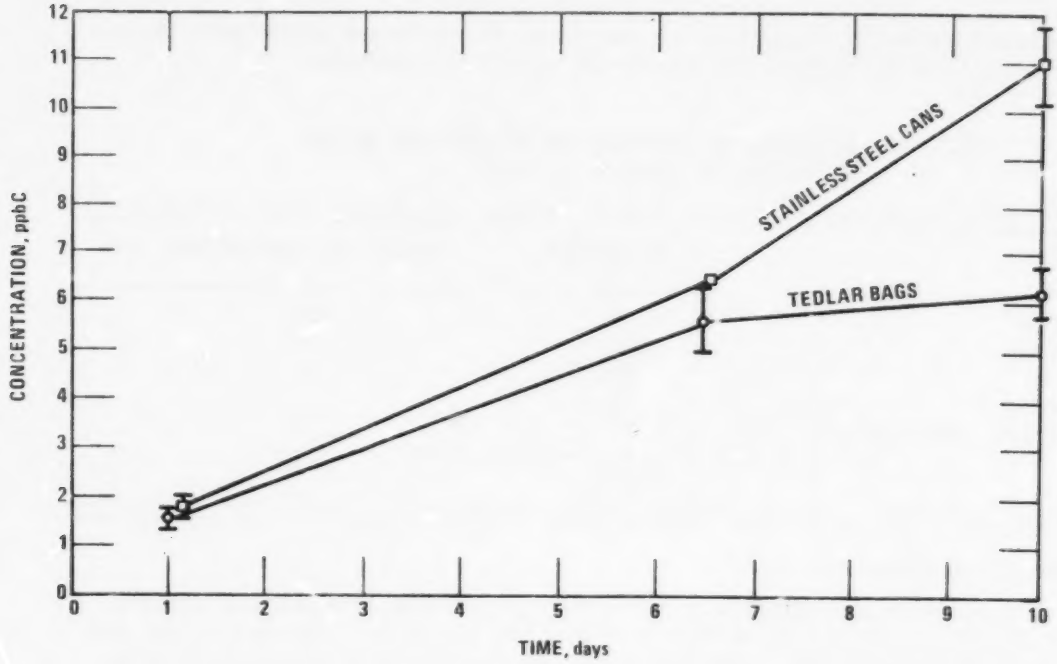

Figure 6. Acetaldehyde concentration versus storage time in stainless steel cans and Tedlar bags.

COMPOSITION OF JONES STATE FOREST NMTHC

Table 5 shows the breakdown of the Jones State Forest NMTHC into hydrocarbon structure categories, of which the paraffins dominate.

TABLE 5. HYDROCARBON COMPOSITION OF JSF AIR ON THE AFTERNOON OF JANUARY 5, 1978

Category	Composition	Median concentration, ppbC
Paraffins	72%	89
Aromatics	18%	22
Olefins	6%	7
Acetylene	2%	3
Vegetative hydrocarbons	2%	3
Total	100%	124

NATURAL GAS COMPOSITION

The percentage composition of Houston commercial natural gas was computed from the analysis results of two samples (Table 6). These natural gas data are used in the later discussion of the sources of Jones State Forest NMTHC.

TABLE 6. COMPOSITION OF HOUSTON COMMERCIAL NATURAL GAS

Compound	Percentage
Methane	90.19 $\pm$ 0.41
Ethane	5.61 $\pm$ 0.36
Propane	2.40 $\pm$ 0.12
N-Butane	0.78 $\pm$ 0.05
Isobutane	0.47 $\pm$ 0.04
N-Pentane	0.28 $\pm$ 0.03
Isopentane	0.28 $\pm$ 0.02

SOURCES OF JONES STATE FOREST NMTHC

An analysis was performed based upon the hydrocarbon to acetylene (C_2H_2) ratios within JSF, Houston ambient air, and two Houston tunnels to determine the sources of Jones State Forest NMTHC. If two assumptions are made: that vehicular emissions are the only significant source of C_2H_2 and that C_2H_2 is unreactive in the atmosphere, then C_2H_2 can be used to trace both auto exhaust and the Houston urban plume. The appropriate ratio of source hydrocarbon to C_2H_2 multiplied by the Jones State Forest C_2H_2 concentration yields the hydrocarbon concentration in JSF due to the particular source. Similar C_2H_2 ratioing techniques have been used by others in the past (9,10,11).

For this analysis to be valid the wind during and somewhat prior to the sampling period at Jones State Forest had to be from the general direction of Houston which is to the south. The wind was indeed from a southerly direction during the entire three-day study; when the can samples were collected on January 5, the mean hourly average wind direction from 10:00 to 16:00 CST was $192^{o} \pm 5^{o}$ at the Texas Air Control Board's Aldine station. The mean hourly average wind speed during the same eight hour period was 21.4 4 $\pm$ 1.7 m sec^{-1} (12).

The data for the analysis of the hydrocarbon to C_2H_2 ratios were from two sources: the can sample results of this report, and Houston metropolitan area and tunnel (Baytown and Washburn) data reported by Lonneman et al. (13) This earlier study consisted of two tunnel samples and 19 ambient samples distributed between Jacinto City to the north, Baytown to the east, Pasadena to the south and the I-45/I-10 interchange to the west. Seven of the ambient samples were collected on a very stagnant day; their NMTHC values ranged from 2.9 to 9.1 ppm.

The hydrocarbon to C_2H_2 ratios of the most abundant compounds observed in JSF were determined for Houston ambient and tunnel air, and JSF air. The methods of the ratio calculations are shown in Appendix B, while the ratios themselves are plotted in bar graph form in Figure 7. The three bars under each group or individual compound represent, from left to right, the compound to acetylene ratio in Houston tunnel air (vehicular emissions), Houston metropolitan air, and JSF air. This bar graph provides a visual basis for explaining the qualitative relationships between the various ratios and the hydrocarbon sources.

If diluted vehicular emissions were totally responsible for the hydrocarbons in JSF then the three lines under each compound would be of nearly equal height. While the paraffins and aromatics do not show this relationship, the olefinic compounds do, suggesting that the predominant source of olefins in JSF is vehicular emissions. The slightly decreasing olefin/acetylene trend indicates that the olefins have reacted somewhat during transport to JSF.

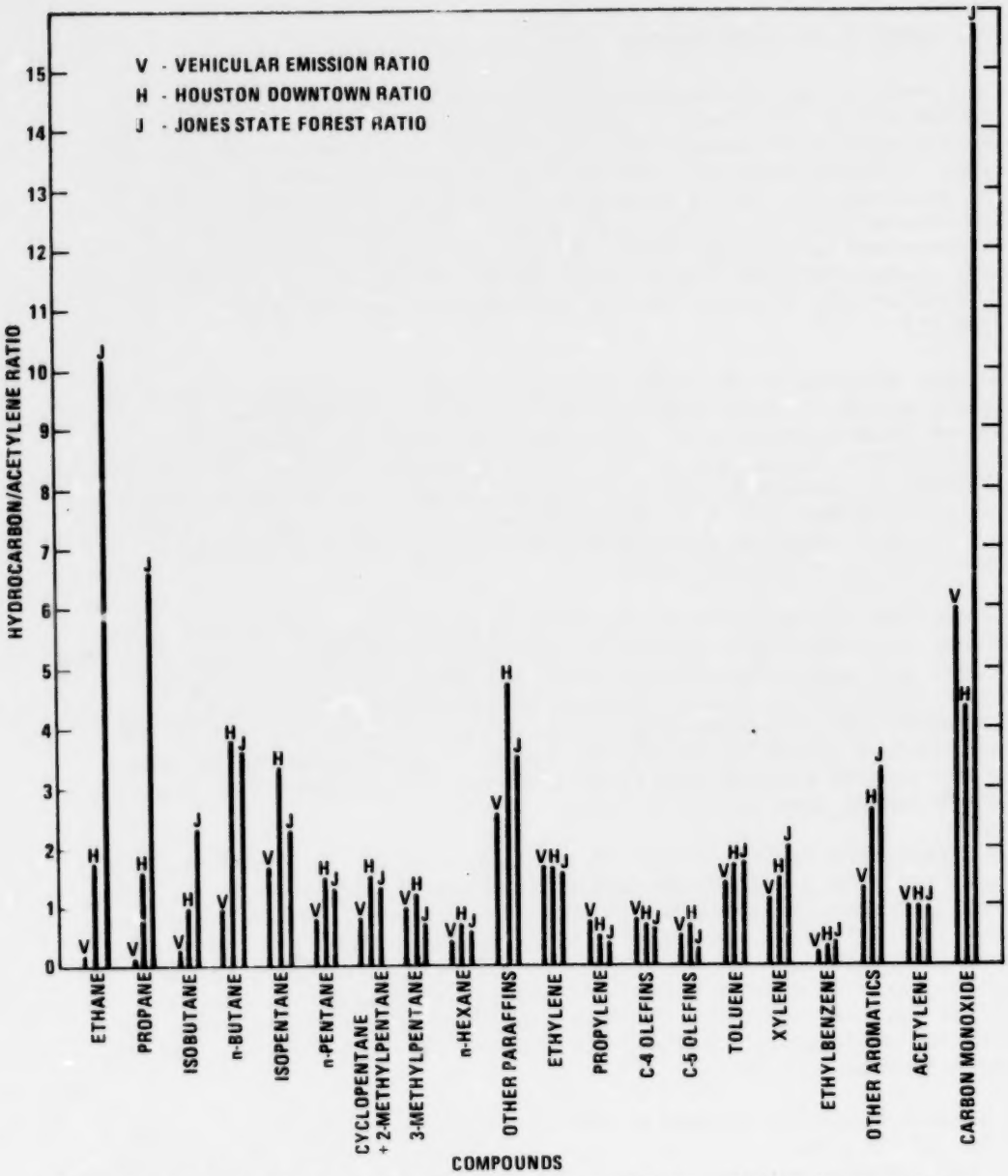

Figure 7. Hydrocarbon-to-acetylene ratios of Houston vehicular emissions, Houston downtown air, and Jones State Forest air.

Hydrocarbon sources other than vehicles would be revealed by lines (hydrocarbon/C_2H_2 ratios) higher than the corresponding auto exhaust ratios. The increased ratios of all of the paraffins and aromatics of Houston air relative to the tunnel air indicate that there are sources of these compounds in Houston other than auto exhaust. In addition, the fact that the ratios of some of the paraffins (ethane, propane, isobutane) are higher in JSF air than in Houston air indicates that the sources of these paraffins are other than Houston or auto exhaust. These sources must be located between the Houston and JSF sampling areas. This area will be referred to hereinafter as "north Houston" and defined as the area between I-610 and the JSF boundary.

The previous graphical analysis suggests three sources for Jones State Forest NMTHC: vehicles, Houston and north Houston. However, fourth source, JSF vegetation, can also be added. The contribution of vegetative sources was determined by direct measurement of the natural hydrocarbons in the JSF samples. The contributions of each of the other three sources were determined by calculations based upon hydrocarbon to C_2H_2 ratios. The Houston and north Houston sources were further subdivided into individual and grouped hydrocarbon contributions. One should note that the Houston and north Houston categories do not include vehicular emission compounds from those areas; these compounds are from sources other than vehicles. The methods of the calculations and error estimation are described in detail in Appendix B; the results are presented in Table 7.

SOURCE ANALYSIS RESULTS

Vehicular emissions comprise 35% of Jones State Forest NMTHC. This percentage is only slightly higher than the vehicular contributions to C_2 to C_5 hydrocarbons determined by McMurray, et al. (14) and Westberg (15) for several sites in the Houston metropolitan area itself.

The Houston metropolitan area hydrocarbons from sources other than vehicles are primarily light paraffins - ethane, propane, butane, pentane. There were also some heavier paraffins and aromatics present. The sources of these compounds could be refinery/industry and/or natural gas. Although the light paraffins are compounds in natural gas, the percentage of the ethane and propane components of the Houston non-vehicular NMTHC of Jones State Forest is too low to represent much natural gas. If the assumption were made that all of the non-vehicular ethane in JSF due to Houston (3.6 ppbC) were from natural gas, then the natural gas concentration in JSF due to Houston would be $3.6 \div 0.57 = 6.3$ ppbC, where 0.57 is the ratio of ethane to NMTHC in Houston natural gas. Of the non-methane hydrocarbons in Houston other than vehicular emissions, no more than 22% ($6.3 \div 29.1$) can be due to natural gas emissions; the rest must be due to refinery/industry sources.

The non-vehicular hydrocarbons emitted between Houston and Jones State Forest (north Houston) are also primarily light hydrocarbons—ethane, propane, isobutane—and some aromatics. In this case the proportions of ethane and propane suggest that the natural gas component of non-vehicular NMTHC in north Houston is higher than in Houston air.

TABLE 7. SOURCES OF JONES STATE FOREST NMTHC

Sources	Compounds	Concentrations±estimated standard error, ppbC Individual	Total	Percent
Vehicles			46.0±8.8	34.6
Houston*				
	n-butane	7.7±1.9		
	propane	4.0±1.0		
	ethane	3.6±0.9		
	isobutane	2.0±0.5		
	n-pentane	2.0±0.7		
	isopentane	1.4±1.2		
	other paraffins	2.7±2.2		
	aromatics	5.7±2.2		
	Total		29.1±9.7	21.9
North Houston*				
	ethane	23.1±5.9		
	propane	13.3±3.7		
	isobutane	3.5±0.9		
	aromatics	2.9±4.3		
	Total		42.8±8.8	32.2
Vegetative hydrocarbons			3.0±0.4	2.2
All			120.9±12.7	90.9
Measured NMTHC			133.0±15.4	100.0
Unspecified NMTHC			12.1±20.0	9.1

* Excluding vehicular emissions

Again, the assumption that natural gas is the source of all ethane leads to a computation that 95% of the non-vehicular NMTHC in JSF from north Houston is natural gas. The use of propane or isobutane for the same computation yields values over 100%. This is strong evidence of very significant natural gas emissions from the north Houston area.

An alternative view of these relationships is to compare the relative compositions of refinery emissions and natural gas to those of Houston and north Houston non-vehicular hydrocarbons. Table 8 compares the light paraffin/ethane ratios of the aforementioned sources. The natural gas ratios were computed from the samples of this study, while the refinery ratios were computed from ambient hydrocarbon concentration data reported

by Westberg, et al. (16). The Houston ratios more closely resemble refinery ratios, while the north Houston ratios more closely resemble natural gas ratios; hence, the primary sources of Houston non-vehicular hydrocarbons in these two areas appear to be refinery emissions and natural gas emissions, respectively.

TABLE 8. COMPARISON OF HOUSTON AND NORTH HOUSTON LIGHT PARAFFIN/ETHANE RATIOS TO THOSE OF NATURAL GAS AND REFINERY EMISSIONS

	Sources			
Compound	Refinery	Houston	north Houston	natural gas
Ethane	1.0	1.0	1.0	1.0
Propane	2.7	1.1	0.6	0.4
n-Butane	3.1	2.1		0.1
i-Butane	1.3	0.6	0.1	0.08
n-Pentane	1.1	0.6		0.05
i-Pentane	1.5	0.4		0.05

There is evidence of industrial activity north of Houston which could be a source of natural gas. The carbon monoxide to acetylene ratio in JSF is much higher than either the vehicular or Houston CO to C_2H_2 ratios, indicating there are sources of CO other than vehicles (e.g. industrial combustion). The hydrocarbon measurements of Westberg, et al. in 1976 at a site north of Houston showed "high aromatic content" (17) which further suggests industrial activity. The concentration of ethane in Jones State Forest unaccounted for by dilution of Westberg's north site air was computed to be 15 ppbC. This suggest that there are considerable sources of ethane between Westberg's north site and Jones State Forest. The source of this ethane could be natural gas emissions.

Although there is strong evidence of natural gas in JSF, the sources are not precisely known. The evidence of industrial activity suggests industrial sources. However geogenic oil and natural gas seeps are known to exist along the east coast of Texas (18), which suggests that the possibility of some geogenic natural gas being present in JSF cannot be excluded.

VEGETATIVE HYDROCARBONS

Jones State Forest is predominantly a loblolly pine forest, but some hardwoods, primarily oak and sweetgum are also present. Alpha-pinene and isoprene are the major emissions of loblolly pine and hardwoods, respectively (19). These are the natural hydrocarbons one would most expect to see at JSF. Lesser emissions one might expect are d-limonene, beta-pinene, Δ^3-carene, and beta-phellanderene (20).

The results of this study were no exception to previous findings by this and other laboratories that ambient concentrations of natural hydrocarbons were in the low ppb carbon range. Only alpha-pinene and isoprene were observed in any of the samples: Isoprene in two and alpha-pinene in fourteen (all but one). The two isoprene measurements were 0.4 and 1.2 ppbC; the mean alpha-pinene concentration (from a range of less than 0.1 to 7.7 ppbC) was 3.6 ± 0.5 ppbC. As Table 6 shows, the natural hydrocarbon contributed to Jones State Forest NMTHC was only 2%.

The diurnal variation of alpha-pinene compared to that of ethane and the wind speed is plotted in Figure 8. The plot shows that the alpha-pinene concentration increases rather sharply at sunset as the nocturnal inversion sets in marked by lowered wind speed. The concentration begins to decrease during the night as the mixing height above ground rises and decreases further during the day after the inversion has broken and wind speed has increased. This diurnal behavior is precisely that which one would expect from a local source such as the pine trees in JSF. In contrast, the ethane concentration shows generally the opposite behavior of alpha-pinene. Its concentration falls as the nocturnal inversion begins, but rises during the day when there is considerable mixing from above. This behavior indicates that the source of ethane is not local, but exists outside of JSF. The peculiar rise of ethane and drop of alpha-pinene during the last 3-hour sampling period was probably due to a breakup of the nocturnal inversion by rain in the night. The diurnal behavior of alpha-pinene indicates that meterological conditions influence the concentration of vegetative hydrocarbons. Daytime meterological conditions of full sun and good mixing render very remote the possibility of vegetative hydrocarbon concentrations rising to levels of photochemical significance.

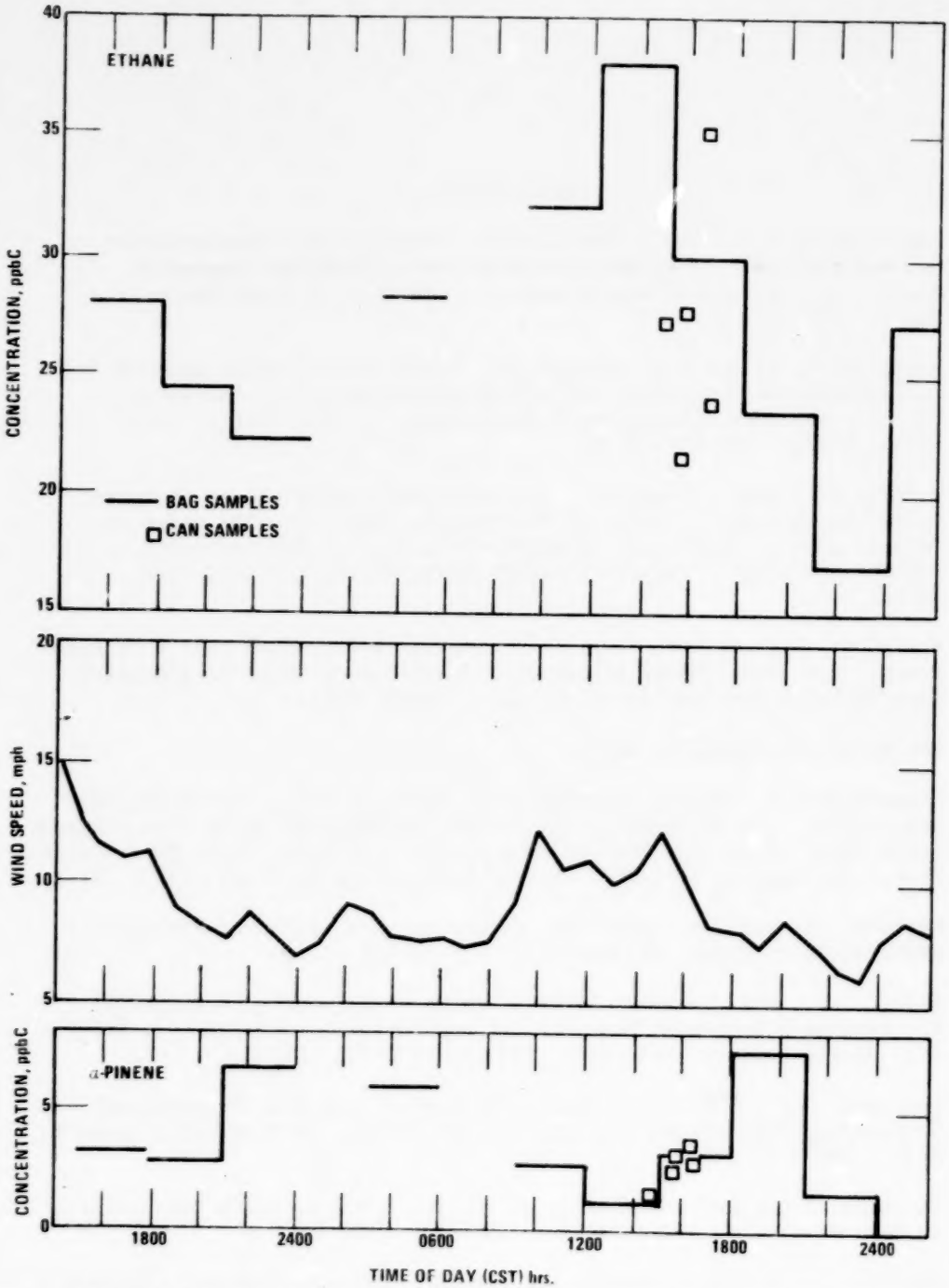

Figure 8. Diurnal variation of α-pinene, ethane, and wind speed at Jones State Forest, January 4 6, 1978.

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APPENDIX A

DETAILED HYDROCARBON, CO DATA SUMMARY

Table A1 gives a complete summary by time and location of the Jones State Forest detailed hydrocarbon, methane, and carbon monoxide data. The blank spaces in the non-methane hydrocarbon section of the table indicate the concentrations below the detection limit of 0.1 ppbC. The CH_4, CO data for the 1/05, 16-18 sample are blank because a lack of sample prevented the analysis. The "1" under location indicates the picnic sampling site, while the "2" indicates the forest interior sampling site (see Figure 2).

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Table A1. JONES STATE FOREST HYDROCARBON AND CARBON MONOXIDE DATA

DATE, 1978	1/04	1/04	1/04	1/05	1/05	1/05	1/05	1/05	1/05	1/06	1/05	1/05	1/05	1/05	1/05
TIME, CST	15-18	18-21	21-24	03-06	09-12	12-15	16-18	18-21	21-24	00-03	1440	1608	1620	1530	1540
LOCATION	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2
	CONCENTRATION, PPBC														
COMPOUND	BAG SAMPLES										CAN SAMPLES				
ACETYLENE	3.6	8.0	9.2	5.0	6.2	2.5	3.6	2.8	1.2	2.8	1.8	3.1	4.0	2.6	2.0
ETHANE	27.9	24.4	22.2	29.3	32.2	38.4	30.0	23.4	17.0	27.2	27.3	35.4	24.1	21.7	27.6
PROPANE	34.9	26.2	32.0	34.4	24.4	12.9	16.1	12.8	15.0	18.8	18.4	18.1	14.5	17.5	15.8
ISOBUTANE	16.1	10.4	14.5	17.1	12.2	9.6	24.2	4.4	7.6	15.2	6.2	6.6	7.6	6.2	5.8
N-BUTANE	18.4	12.4	36.4	28.4	22.0	13.6	16.4	31.6	49.6	12.0	11.2	8.6	10.4	9.7	8.2
ISOPENTANE	14.8	9.9	14.7	15.0	14.1	7.6	10.6	21.9	49.6	15.0	5.9	5.8	5.4	7.0	6.0
N-PENTANE	9.3	4.9	9.7	12.9	9.9	8.6	17.9	21.8	16.0	12.2	4.7	3.3	3.4	4.6	3.6
CYCLOPENTANE	.9	.6	1.1	1.7	1.3	1.8	1.5	4.1	6.1	1.1	.6	1.0	.6	.3	.3
2-METHYLPENTANE	3.9	2.4	4.0	5.6	4.5	6.3	3.1	19.5	13.6	2.5	1.2	1.4	1.1	.9	1.7
3-METHYLPENTANE	1.9	2.3	3.7	3.0	4.1	2.0	3.4	14.9	10.9	2.4	.9	1.0	.0	.9	.9
4-METHYLPENTANE	.1			.2			.1	.5	.2	.4				.3	
METHYLCYCLOPENTANE	3.1	1.9	9.8	3.9	4.4	3.1	3.1	6.7	7.4	2.7					
UNKNOWN C6	1.0	.6	1.1	1.8	1.3	1.9	2.1	3.5	2.8	1.1	.6	.5	.5	.3	.3
N-HEXANE	3.6	2.2	3.6	5.9	5.6	2.9	3.1	17.7	8.5	4.3	2.1	1.5	1.6	2.2	1.5
UNKNOWN C6	.2	.1	.1	.2	.1		.1	1.2	2.6	1.2				.7	
CYCLOHEXANE	1.1	2.0	1.4	1.7	3.3	2.6	1.6	3.1	1.1	1.6	1.5	1.1	.9	.3	1.0
UNKNOWN C6								.6	1.8						
2,3 DIMETHYLPENTANE	.6	.9	.5	.8	1.5	2.6	2.4	3.1	11.5	2.0				.6	.6
2,4 DIMETHYLPENTANE									10.6	.9					
1C3 DIMETHYLCYCLOPENTANE	.6	.6	.4	.4	1.7	.6	.7	1.1	.3	1.0	.8	.6	.6	.3	.3
1T3 DIMETHYLCYCLOPENTANE	.2		1.5	.4	.9	2.1	1.2	1.4	.9	1.0			.2	.3	.3
2-METHYLHEXANE	1.9	.5	.9	1.7	2.7	4.6	4.6	6.4	4.8	2.8	.5	.4	.4	.3	.6
3-METHYLHEXANE	2.1	3.0	1.1	1.6	3.2	5.8	5.3	8.7	4.0	5.0	.7	.8	.7	2.1	1.5
UNKNOWN C7	4.5	1.5	1.9	3.6	4.5	1.3	.6	.6	.7	1.0				.3	
UNKNOWN C7	1.3		2.9	3.9	5.3	2.0	4.0	6.3	6.0	10.0		1.4	2.4	16.9	3.8
METHYLCYCLOHEXANE	3.0	1.6	1.3	2.4	4.5	7.9	9.2	5.3	5.0	9.3	2.6	3.8	2.7	2.4	4.1
N-HEPTANE	3.1	1.9	2.2	2.3	3.1	3.9	7.1	8.5	3.2	6.8	1.1	1.4	1.2	1.5	.7
2,2,4 TRIMETHYLPENTANE	.5		1.5	.7	1.8	2.1	1.8	4.4	16.7	1.5			.3	.6	1.8
N-NONANE	1.5	2.6	2.7	.6	1.0	.9	2.6	1.0	1.8	11.1	.5	.5	.6	1.1	.8
N-DECANE	5.0	4.2	1.4	2.1	.4	2.8	4.5	4.3	3.1	27.7	1.2	.8	.9	1.5	1.6
ETHYLENE	16.2	5.7	13.8	8.9	15.6	4.0	5.0	3.8	8.9	13.4	2.7	6.3	3.7	7.2	4.2
PROPYLENE	7.2	4.6	8.4	6.6	6.4	1.9	2.0	3.2	1.6	5.6	1.0	1.0	1.0	6.8	1.0
ISOBUTYLENE	4.6	1.2	6.2	3.3	5.7	1.7	2.8	3.6	3.5	3.3	1.0	.6	.3	5.4	.1
T-BUTENE-2	5.2	3.8	10.0	3.5	1.0	5.1	4.1	2.2	3.5	2.0	2.3	.6	.3	2.3	.1
C-BUTENE-2, BUTADIENE	2.6	2.5	3.4	2.7	4.9	1.7	1.4	2.4	4.6	6.5	.3	.7	.6	.1	.1
2-METHYLBUTENE-1	.3	.2	.2	.2	.3	.2	.2	1.1	3.2	.5		.1	.1	.4	.1
2-METHYLBUTENE-2	.1	.1	.2	.1	.3	.3	.2	1.6	7.1	.6					
PENTENE-1	.6	.1	.4	.6	.4	.2	.3	.8	1.5	.4		.1	.1	1.5	.1
T-PENTENE-2	.3	.2	.2	.2	.3	.2	.2	3.8	2.8	2.1		.1	.1	.2	.1
C-PENTENE-2									1.7			.1	.4		.4
HEXENE-1	.1			.1	.1		.1	.1	.1	1.4					
T-HEXENE-3	.1				.1	.4	.4	1.4	1.9	.2					
C-HEXENE-2								1.8	3.3	.8					
TOLUENE	10.4	11.3	9.4	9.1	10.0	9.2	25.5	25.6	14.0	91.9	4.7	4.2	4.3	9.4	9.8
UNKNOWN C7	4.0	4.8	4.2	3.5	4.1	3.8	6.8	5.8	2.7	4.0	3.8	2.2	.4	14.6	1.9
UNKNOWN C8	1.3	2.9	1.9	1.2	.4	.3	.6	1.7	.5	1.1	.1	.2		2.2	.6
ETHYLBENZENE	3.9	2.7	3.3	1.8	2.4	1.6	6.0	2.9	2.3	10.4	1.0	1.1	1.0	.8	1.6
P-XYLENE	1.2	2.0	1.3	1.0	1.4	.8	1.6	2.0	1.7	16.1	.2	.3	.6	.2	.8
M-XYLENE	5.4	6.4	4.4	3.3	4.2	3.0	8.3	6..	6.0	48.3	2.7	1.3	2.1	.9	2.7
O-XYLENE	2.5	5.5	5.3	2.3	3.3	2.6	5.1	3.6	3.1	24.8	2.4	2.3	.2	7.6	3.1
UNKNOWN C8				.6										2.4	
ISOPROPYLBENZENE	.5	1.3	.7	1.2	.8	.8	1.7	1.5	.7	16.3	.6	7.7	6.5	8.5	18.7
UNKNOWN C9	1.0	1.8	3.1	1.5	.8	1.4	2.0				.9	1.8	2.8	5.3	2.2
N-PROPYLBENZENE	.5		.1		.8	1.9	2.1	2.8	.4	4.4			.2	.9	.9
3,4 ETHYLTOLUENE	3.0	3.3	3.0	1.1	2.0	1.4	3.3	2.5	1.4	17.2	.3	.3	.2	.1	1.2
UNKNOWN C9				1.5		2.2		1.4						1.8	
1,3,5 TRIMETHYLBENZENE	1.0	2.5	3.6	.1	1.1	1.0	1.4	1.5	.3	12.8	1.6	.3	.4	.1	.3
1,2,4 TRIMETHYLBENZENE	.7	5.7	2.1	.8	2.1	1.0	2.6	1.4	.8	34.7	.5	.6	.4	.3	.4
O-ETHYLTOLUENE	.1	1.7	3.3		1.0	.2	1.0	1.0	.1	5.7					
UNKNOWN C9														9.5	
ACETALDEHYDE	8.9	6.9	8.5	7.2	16.9	7.0	15.7	18.7	7.0	4.4	12.0	10.7	3.4	56.2	7.4
ACETONE	7.1		16.0	2.9	7.1	5.7	19.4	3.0	4.7	3.0	5.4	7.9	4.9	7.0	6.9
PROPIONALDEHYDE											3.9	14.2	1.8	39.9	34.3
ISOPRENE										1.2		.4			
ALPHA-PINENE	3.2	2.9	6.8	5.9	2.7	1.3	3.4	7.7	1.7		1.7	3.6	3.0	2.7	3.4
SUM NMHC	257.3	205.4	301.9	246.6	272.6	211.1	304.5	356.9	361.3	530.9	138.9	165.8	123.9	297.2	193.2
METHANE (PPM)	2.09	2.10	2.11	2.12	2.24	2.28		2.06	1.97	1.99	2.18	2.20	2.19	2.15	2.14
CARBON MONOXIDE (PPM)	.51	.55	.65	.77	.82	.55		.57	.39	.88	.69	.39	.48	.37	.42

APPENDIX B

SOURCE CONTRIBUTION CALCULATIONS

In this appendix the methods are shown for the calculations of the source contributions to JSF and their standard errors (see Table 7).

The vehicular and Houston hydrocarbon to acetylene ratios, R, were estimated by the formula:

$$R = \frac{\Sigma[hc]}{\Sigma[ac]} \qquad \text{(Eq. 1)}$$

where [hc] is hydrocarbon concentration and [ac] is acetylene concentration. The JSF ratios were estimated by the formula:

$$R = \frac{[\bar{\bar{hc}}]}{[\bar{\bar{ac}}]} \qquad \text{(Eq. 2)}$$

where $[\bar{\bar{hc}}]$ was the median of the five can samples. Since the number of samples was small, it was decided that the median rather than the mean, in this case was a better measure of central tendency (21).

The vehicular component of JSF air was determined by multiplying the mean tunnel NMTHC/C_2H_2 ratio times the JSF mean C_2H_2 concentration:

$$[NMTHC]_V = R_V[\bar{\bar{ac}}]_J \qquad \text{(Eq. 3)}$$

The Houston component for individual hydrocarbons was determined in like manner:

$$[hc]_H = R_H[\bar{\bar{ac}}]_J \qquad \text{(Eq. 4)}$$

The non-vehicular contribution due to Houston was determined by subtraction:

$$[hc]_{H,NV} = [hc]_H - [hc]_V \qquad \text{(Eq. 5)}$$

$$= R_H[\overline{\overline{ac}}]_J - R_V[\overline{\overline{ac}}]_J \qquad \text{(Eq. 6)}$$

$$= (R_H - R_V)[\overline{\overline{ac}}]_J \qquad \text{(Eq. 7)}$$

The non-vehicular contribution due to north Houston was

$$[hc]_{NH,NV} = (R_J - R_H)[\overline{\overline{ac}}]_J \qquad \text{(Eq. 8)}$$

Equations (3), (7), and (8) were the working equations for the source contribution calculations of Table 7.

The standard errors of the source calculations were determined by propagation of errors methods described by Baird (22). The variances of hydrocarbon contributions were estimated from the variances of the hydrocarbon/acetylene ratios and the mean acetylene concentration. Determination of the variances of the hydrocarbon/acetylene ratios was by the formula:

$$V_R = \frac{\Sigma[hc]^2 - 2R\Sigma([hc][ac]) + R^2\Sigma[ac]^2}{n(n-1)[\overline{\overline{ac}}]^2} \qquad \text{(Eq. 9)}$$

which is a rearrangement of Cochran's formula 2.34 (23). The variance of the mean acetylene concentration is

$$V_{Ac} = \frac{\Sigma([ac]_i - [\overline{\overline{ac}}])^2}{n(n-1)} \qquad \text{(Eq. 10)}$$

The variance of the product of R times $[\overline{\overline{ac}}]$ is

$$V_{HC} = V_R[\overline{\overline{ac}}]^2 + V_{Ac}R^2 \qquad \text{(Eq. 11)}$$

and the estimated standard error is

$$S_{HC} = (V_{HC})^{1/2} \qquad \text{(Eq. 12)}$$